2. VOLATILITY OF ORGANIC COMPONENTS OF SELECTED MATERIALS

2.1. Objective

During the years when nuclear weapons compounds were manufactured at Rocky Flats Environmental Technology Site (RFETS), carbon tetrachloride (CCl_4) was used as a lubricant for machining; and chloromethane (CH_3Cl), or methylene chloride (CH_2Cl_2, also called dichloromethane), and Freon-113 (CCl_2F-$CClF_2$) were used as degreasing fluids. Waste materials contaminated with these chemicals, as well as with methyl chloride (CH_3Cl) and vinyl chloride (CH_2=CHCl), were placed in drums and sent to storage. The present need is to use cryogenic grinding to homogenize contaminated wastes, while minimizing the release of organic species.

In order to determine whether volatile organic components (VOCs) of five selected materials were released during the shredding and mixing processes when these processes are performed at a temperature of –40°C, we sprayed both materials and equipment with liquid nitrogen (LN_2) before shredding and mixing. Gas and metal thermocouples installed throughout the system ensured that constant low temperatures were maintained as needed. The temperature of –40°C is the temperature guaranteed by industrial warranty on the equipment for cryogenic operations: below this temperature, standard bearings and other components must be replaced with cryogenic components. Thus, these tests would determine one of the design criteria (the desired operating temperature) for the shredder/mixer system.

Because we knew the characteristics of the VOCs being tested, effects of the grinding process could be determined by comparing pre- and post-grinding samples. However, we also explored characteristics of VOCs that were present in the mixed-matrix materials of concern. The mixed matrix represented actual expected composition of material in storage.

2.2. Equipment Design and Selection

When the procurement of a commercial shredder capable of meeting experimental schedule and budget needs proved impossible, we procured an off-the-shelf garden shredder—the Snapper—and modified it to meet experimental requirements. We replaced the 8-hp gasoline motor with a 10-hp electric motor that featured a motor-speed controller. We converted the original drive to a belt-and-sprocket drive and geared it to operate at maximum shredder speed at full controller power. The manufacturer's recommended operating speeds were in the 1100–1800 rpm range. We removed the chipper part of the shredder and moved the bearings away from the cooled areas of the shredder. We sharpened the leading edges of the "hammers" and modified the upper and lower funnels. We sealed the unit and strengthened its ability to accommodate thermal loads. We assembled and shock-mounted the motor and shredder on a movable stand. We instrumented the shredder with thermocouples and gas sampling ports and then insulated it.

The mixer used in the mixing tests described in Section 1 was instrumented, insulated, and incorporated in the output end of the shredder. Figure 2-1 shows the final shredder/mixer assembly.

A Hewlett-Packard HP 3852 scanner, a Macintosh computer, and LabVIEW© software (Fig. 2-2) monitored temperatures during the testing. We used an Inficon model 200 Residual Gas Analyzer (RGA) with supporting vacuum system (Fig. 2-3) to do on-line sampling for the volatile organic compounds. A Volatile Organic Sampling Train (VOST) collected the gas samples on thermal desorption tubes (Figs. 2-4 and 2-5), which were sent to the analytical chemistry group for gas analysis.

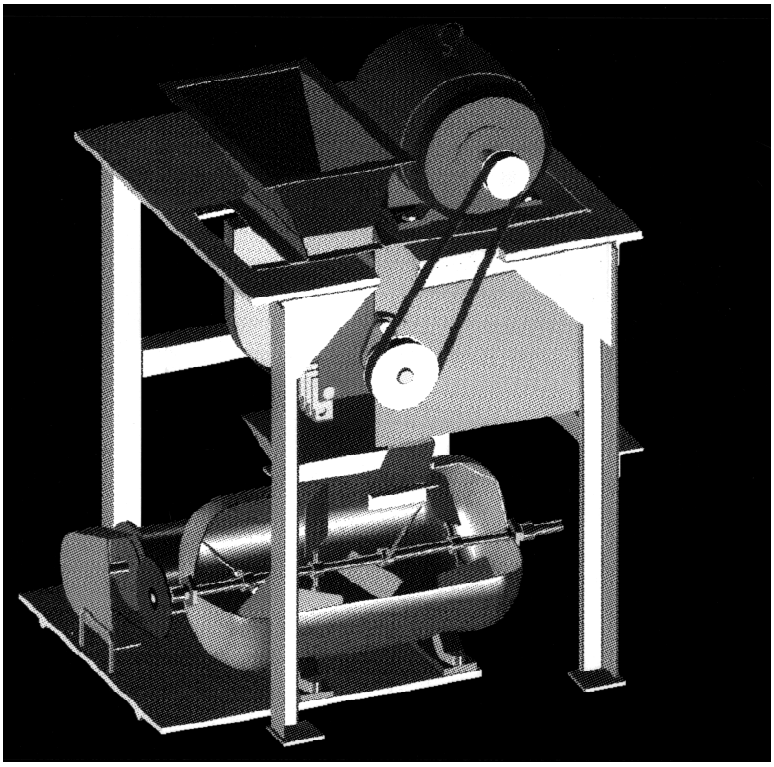

Fig. 2-1. Shredder and mixer assembly.

Fig. 2-2. Instrumentation system.

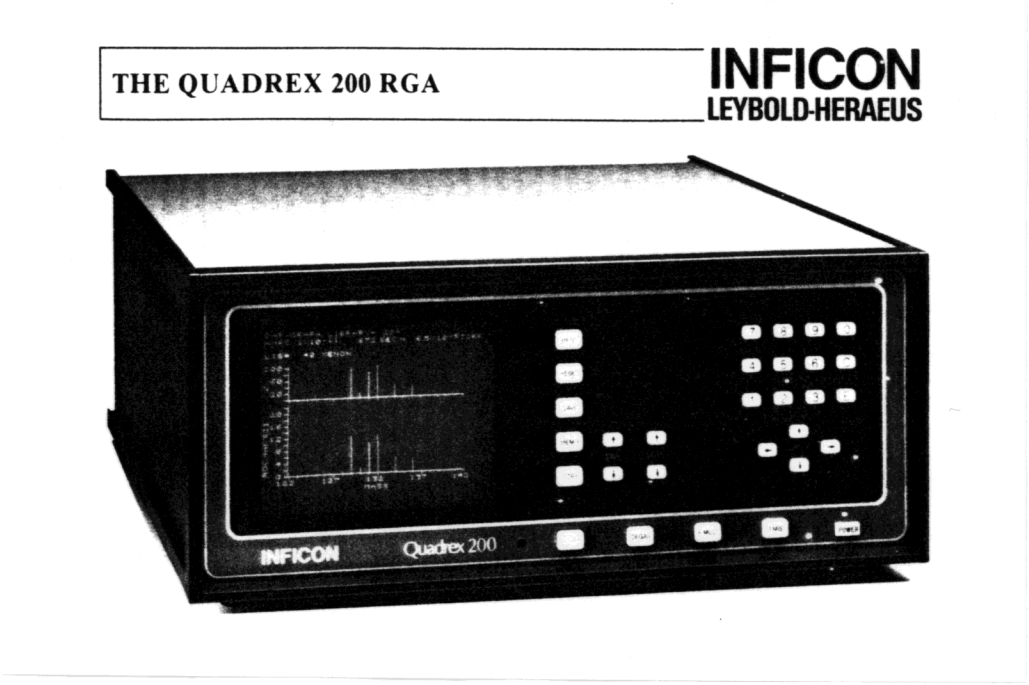

Fig. 2-3. Inficon Model 200 Residual Gas Analyzer (RGA).

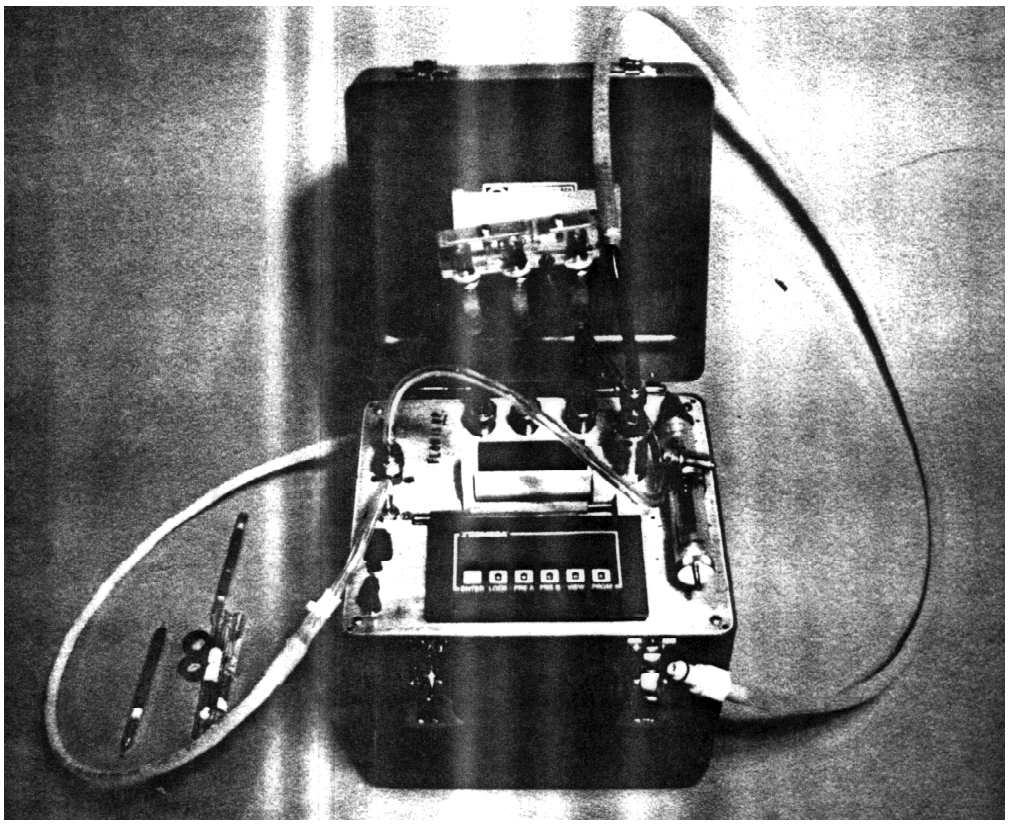

Fig. 2-4. Volatile Organic Sampling Train (VOST).

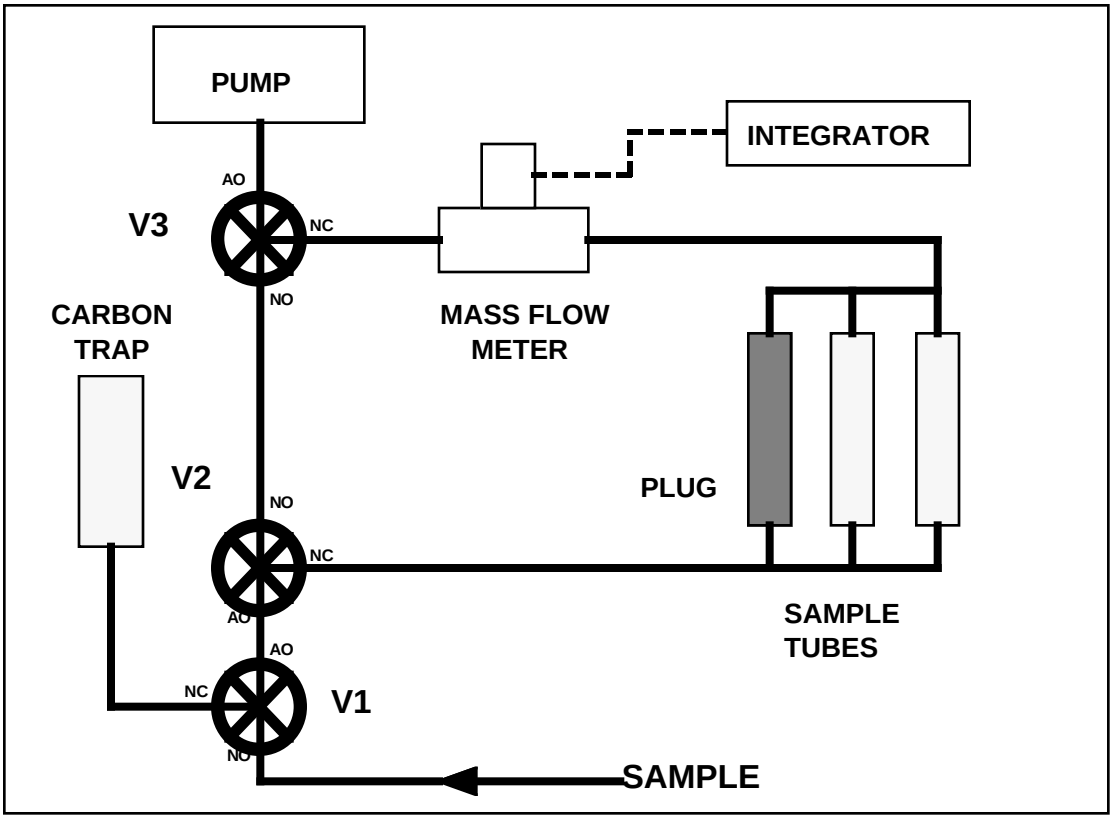

Fig. 2-5. Schematic of the VOST

2.3. Materials Studies

The volatility of the various compounds being examined made it difficult for us to simulate their storage conditions at RFETS. However, by designing a test plan around organic solvents known to exist in the wastes, we hoped to gather significant information for designing a cryogenic grinding system that would facilitate the characterization of solvent-containing wastes in the RFETS drums.

Both CCl_4 and CH_2Cl_2 are members of the series of chlorinated methane molecules that include CH_2Cl_2 or CH_3Cl, and trichloromethane, or chloroform ($CHCl_3$). In general, the vapor pressure of the species increases with the number of hydrogen atoms that are present in the molecule. For example, the vapor pressure of CH_2Cl_2 is 12 torr at –40°C, and the vapor pressure of CCl_4 is 2 torr at –40°C. Because of the significant difference in the vapor pressure between the two species, the effect of cryogenic grinding on the volatility of the organic species will be more pronounced if CH_2Cl_2 is the contaminant.

CH_2Cl_2 is a liquid at room temperature, boils at 40°C, and freezes at –95°C. The vapor pressure ranges from 12 torr at –40°C to 422 torr at 25°C. Actual CH_2Cl_2 vapor pressure observed in these studies is dependent on both the system temperature and the CH_2Cl_2 thermodynamic activity. CH_2Cl_2 is an excellent degreasing agent. Therefore, as it becomes contaminated with grease, its vapor pressure decreases because of the chemical interaction between the CH_2Cl_2; and the grease lowers the thermodynamic activity of the CH_2Cl_2.

The plot in Fig. 2-6 covers a wide range of melting and boiling points for the four solvents of interest here (CH_3Cl, CH_2Cl_2, CCl_4, and CCl_2F-$CClF_2$ [R113]) and illustrates the vapor pressure vs temperature characteristics for these materials as presented in the literature. The concern for operating temperature in the cryogenic grinder is based on the volatility of the solvents; volatility is reflected in the vapor pressure of the various solvent species.

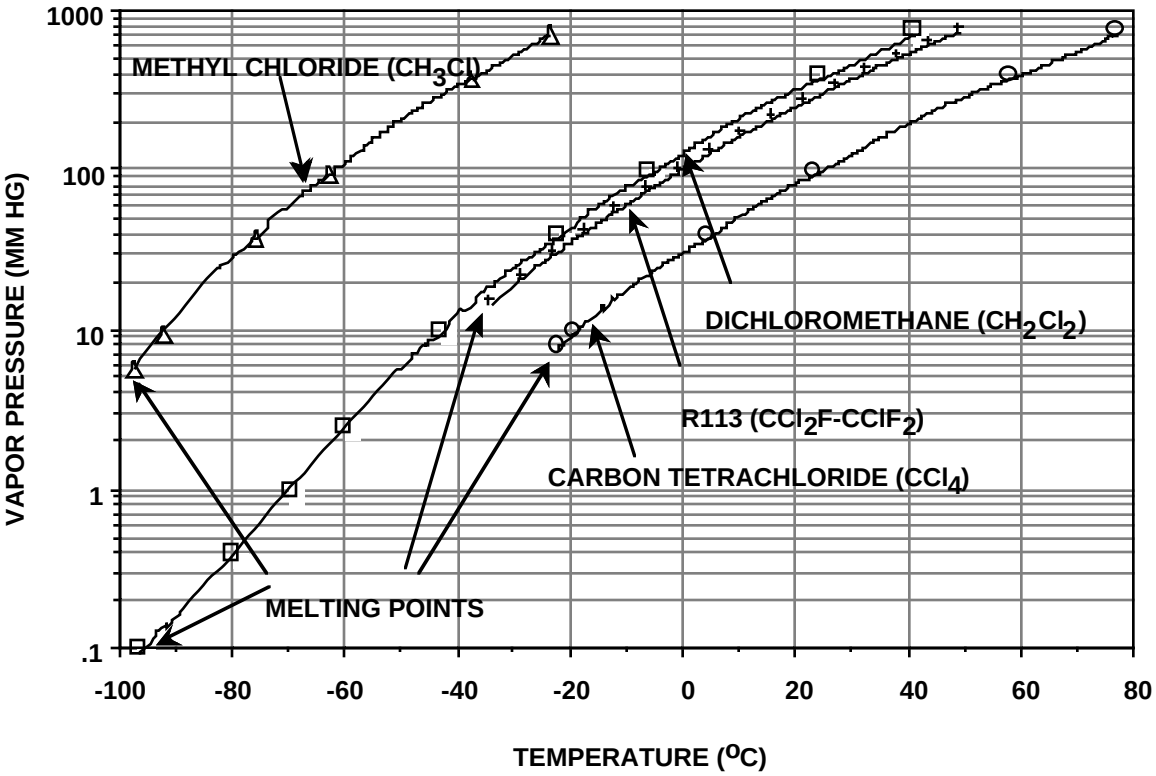

Fig. 2-6. Vapor pressure vs temperature for solvents of interest in Rocky Flats Environmental Technology Site (RFETS) contaminated wastes.

The vapor pressure of these four solvents is extremely high at room temperature, 25°C. Atmospheric pressure is 760 torr at sea level, but the atmospheric pressure at both Los Alamos National Laboratory (LANL) and RFETS is significantly lower. Furthermore, even at –40°C vapor pressures of these solvents is significant. Therefore, even though the boiling points of the different solvents vary significantly—for example, CH_3Cl has a much lower boiling point (–24.2°C) than CH_2Cl_2 (+40°C)—the concern about the escape from the matrix materials of components that have boiling points above room temperature remains significant. In addition, a solvent such as CH_3Cl, which has a low boiling point, also has a significant vapor pressure of 10 torr below –90°C; thus, one does not contain such solvents at –40°C. Interestingly, trichloroflouroethane R113 (CCl_2F-$CCIF_2$ [R113]) is very much like CH_2Cl_2 in its vapor pressure characteristics; however, at its melting point of –34°C, R113 has a significant vapor pressure of 16 torr. This report provides data about the effect

of the oily matrices on the volatility of the solvent they contain.

CH_3Cl was removed from consideration because of the difficulty of attempting to spike the material with this solvent and then evaluate that material. CH_3Cl is a high-pressure gas at room temperature and would be difficult to contain within any matrix.

2.4. Experimental Test Plan

To develop a database reflective of the performance and capability of the equipment and materials, we conducted the experimental test in three steps: material evaluation, mixed-matrix testing, and shredder testing.

2.4.1. Materials Evaluation

After choosing CH_2Cl_2, CCl_4, and $CCl_2F\text{-}CClF_2$ (R113), as test materials, we used the experimental test setup shown in Fig. 2-7 to evaluate the response and sensitivity of the equipment. The RGA recorded the signal for the partial pressure of the volatile gas that was mixed with air at atmospheric conditions (pressure of 590 torr and temperature of 22°C). The volatile gas was placed in the 4.3-L control-volume sample container, which was not sealed hermetically but could be evacuated to clean the system of all gases. For all tests, we obtained samples as follows. We heated the metal line between the control volume and the sampling valve to at least 60°C. We adjusted the sampling valve to regulate the total pressure in the RGA sensor to 3.5×10^{-4} torr. We used the vacuum pump to evacuate the sample line at valve VV with the sampling valve VS closed. We closed valve VV, opened atmospheric valve VA, opened sampling valve VS, then closed VA. This process enabled us to extract a gas sample from the control-volume sample container at atmospheric pressure, while maintaining "dynamic" equilibrium between the air and the organic materials. We repeated this process three times, and on the third time the signal on the RGA was read and recorded. We then repeated the process a fourth time and read the signal intensity again in order to verify that there was no significant change. We arrived at the same numbers the third and fourth times.

We used the setup illustrated in Fig. 2-7 to determine the response of the RGA to the three materials. We placed small quantities of liquid in the control-volume sample container at room temperature and obtained spectral responses for the three materials. Figure 2-8 is the spectral response of the RGA for CH_2Cl_2, and Fig. 2-9 is an expanded view of the organic molecule that fragments into various species detected on the RGA at smaller mass numbers. Figure 2-10 is the spectral response of the RGA for $CCl_2F\text{-}CClF_2$ (R113), and Fig. 2-11 is an expanded view of the predominant peak at mass 101. Figure 2-12 is the spectral response of the RGA for CCl_4, and Fig. 2-13 is an expanded view of the predominant peak at mass 117.

The naturally occurring isotopic ratio for chlorine is about 75% ^{35}Cl and 25% ^{37}Cl. Because of this phenomenon, when observing mass spectra of chlorine molecules, there will be a 3:1 ratio in spectral peaks shifted by two mass units. For example, in Figs. 2-8 and 2-9 the mass of 49 represents $CH_2{}^{35}Cl$ and $C^{37}Cl$. Because of this ratio phenomenon, the signal amplitude at mass 49 is dominated by $CH_2{}^{35}Cl$ and not $C^{37}Cl$. This finding also considers the fact that ion fragmentation is dominated more by $CH_2{}^{35}Cl$ than by $C^{35}Cl$. Moreover, there is an isotopic shift for $CH_2{}^{35}Cl$ and $CH_2{}^{37}Cl$ at masses at 49 and 51 respectively, the shift being dominated in the ratio of mass 25 to 37.

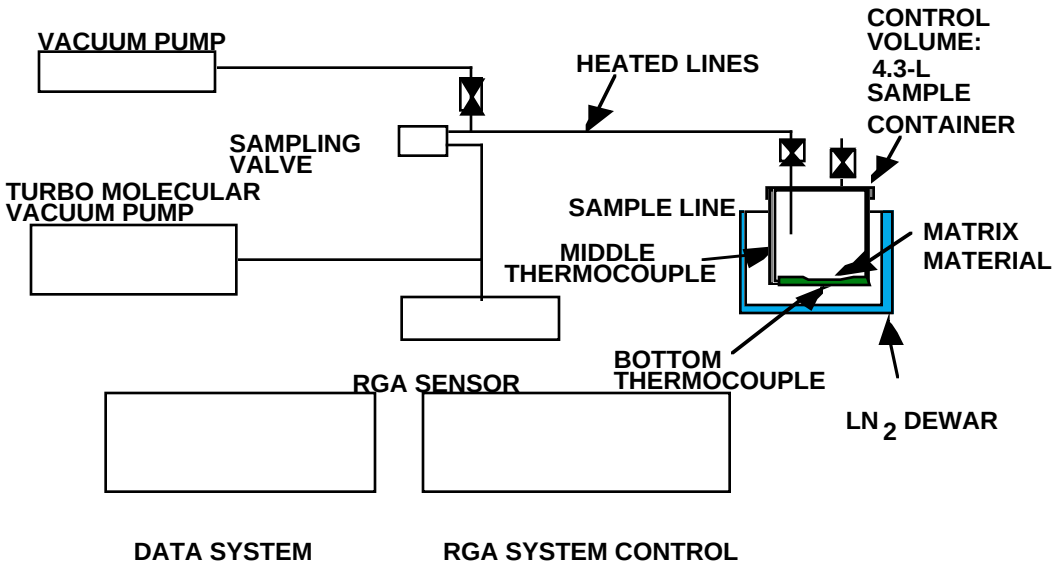

Fig. 2-7. System setup for testing volatility of solvent-contaminated materials at RFETS.

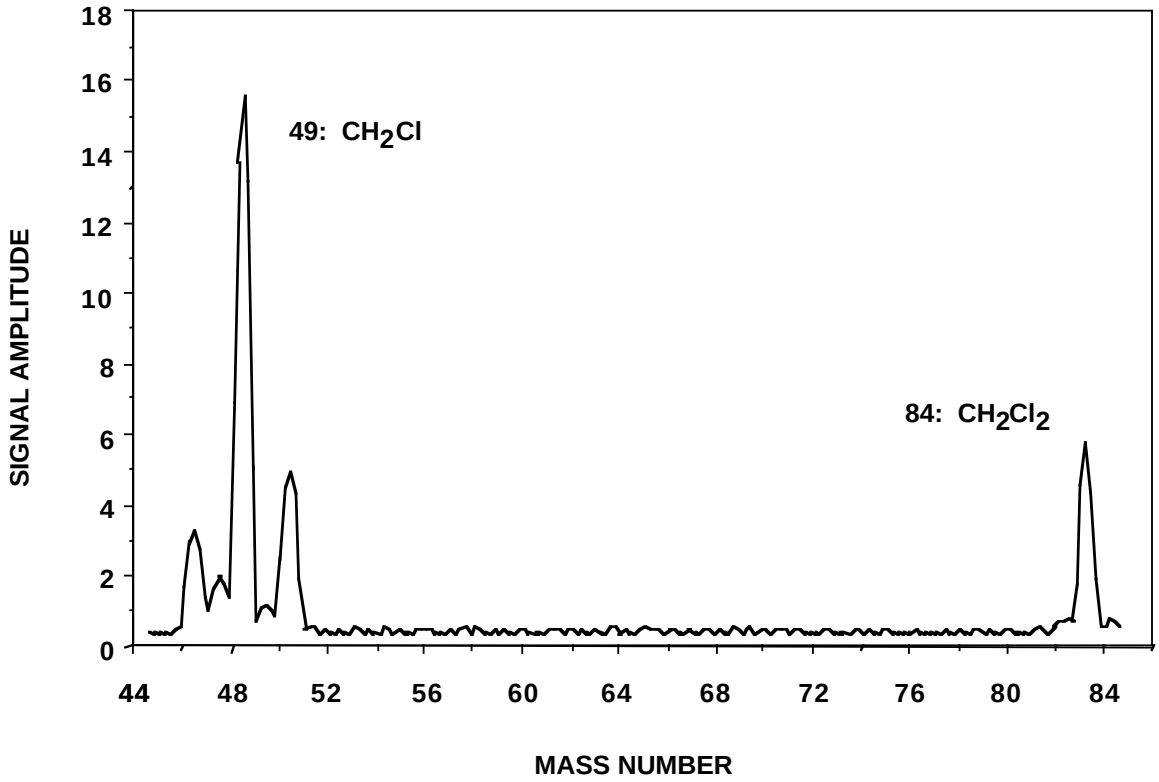

Fig. 2-8. Spectral signal for methylene chloride (CH_2Cl_2). See text for explanation of mass spectrum.

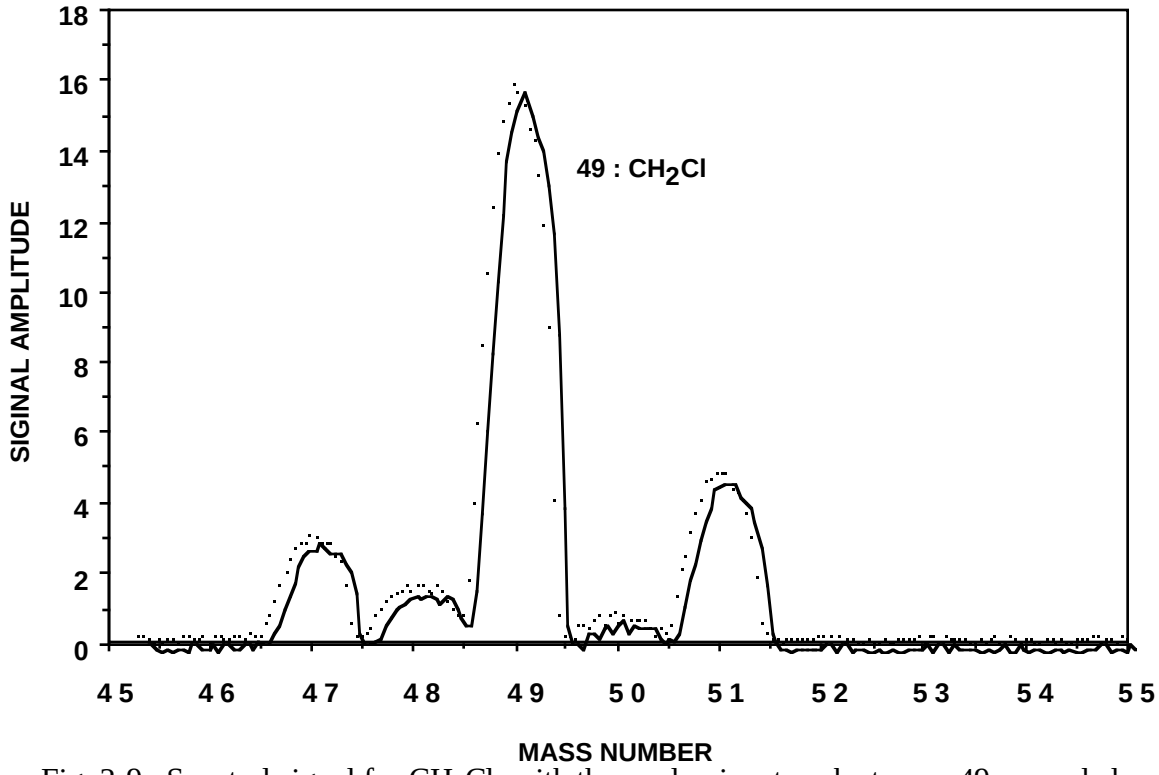

Fig. 2-9. Spectral signal for CH_2Cl_2 with the predominant peak at mass 49 expanded.

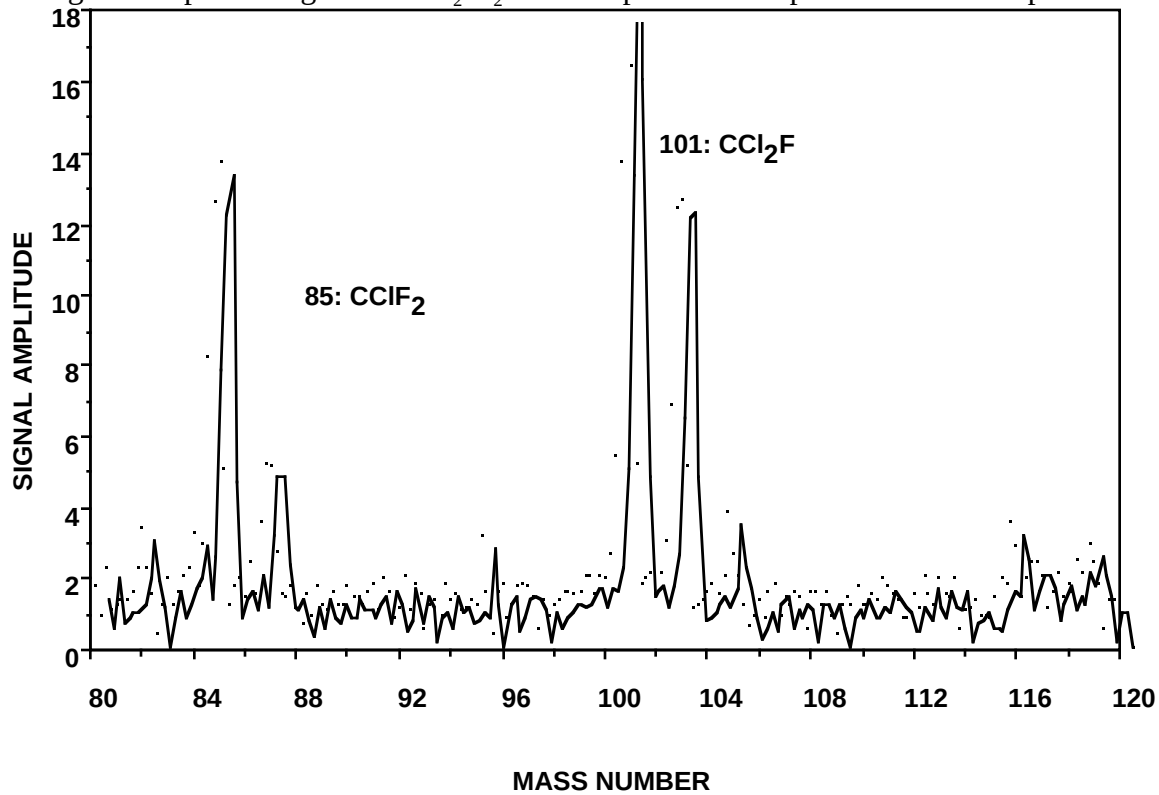

Fig. 2-10. Spectral signal for trichlorofluoroethane (CCl_2F-$CClF_2$ [R113]). Total signal at mass 101 is not shown.

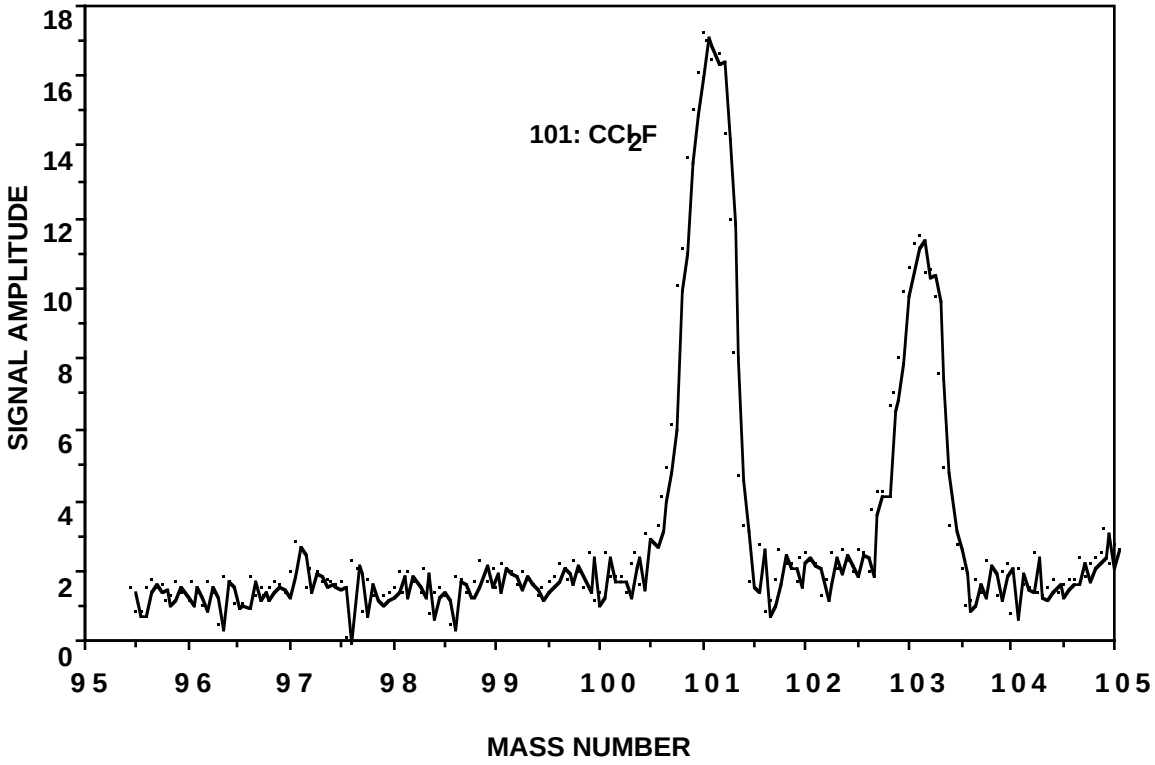

Fig. 2-11. Spectral signal for CCl_2F-$CClF_2$ with predominant peak at mass 101 expanded.

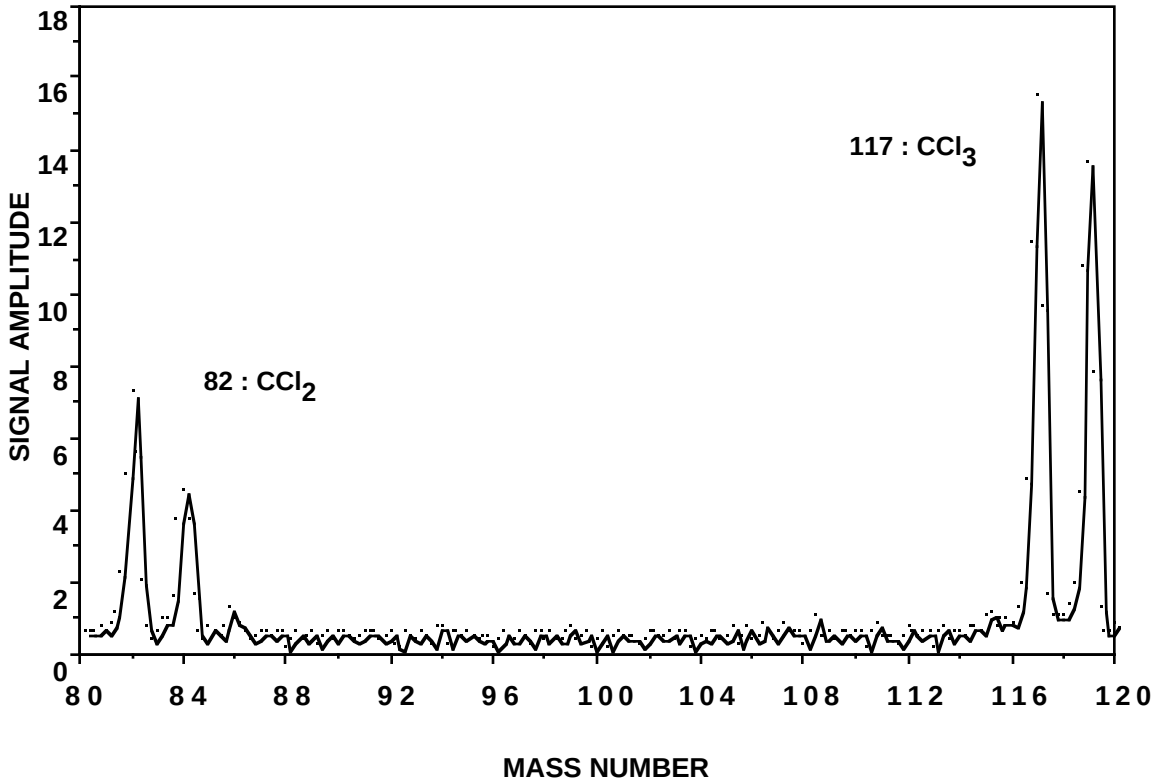

Fig. 2-12. Spectral signal for carbon tetrachloride (CCl_4).

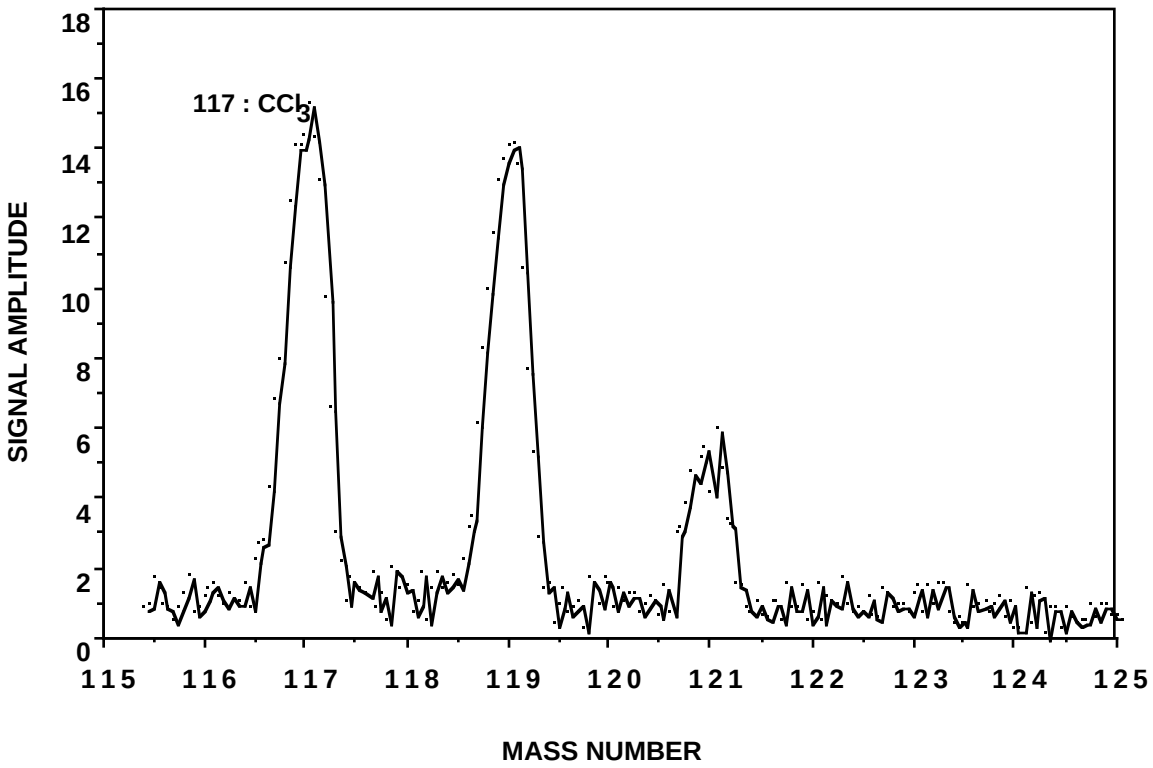

Fig. 2-13. Spectral signal for CCl_4 with the predominant peak at mass 117 expanded.

Using the setup shown in Fig. 2-7, we conducted a set of tests on the organic solvent gases (mixed only with air) and evaluated the RGA response with these gases at reduced temperatures. We placed a small quantity of pure liquid at the bottom of the control-volume sample container and reduced the temperature by chilling the bottom of the container to less than –100°C. We regulated the temperature of the sample by first chilling an LN_2 dewar and then placing the instrumented sample container in the dewar. For the three materials studied, we reduced the temperature to at least –100°C. We allowed air to enter the central volume in order to maintain atmospheric pressure when reducing the temperature. The temperature of the control-volume sample container was slowly increased by injecting small quantities of room-temperature air at the bottom of the dewar. To sample for each data point, we followed the procedure described in Section 2.4.1. We allowed the temperature of the materials to reach thermal equilibrium, and we monitored temperature by placing thermocouples on the bottom and side of the control-volume sample container.

The results of those tests are shown in two formats. Figure 2-14 shows the signal amplitude as a function of temperature for the predeominant mass peaks of the compounds; and Figs. 2-15, 2-16, and 2-17 compare the experimental data we acquired with data in the literature. We compared the vapor pressure data of the volatile organic materials in the form of 1/T vs log P with 1/T vs the log of the RGA response multiplied by the sample temperature. In these figures, the slope of the line indicates whether the tests were conducted in equilibrium conditions. As shown in the plots, the slopes are not the same, although the procedures used were being developed for sampling during the shredding process. As expected, our data differ from data in the literature. We tried to emulate the method of measurements as would be done in the actual shredding test. Data in the literature were obtained at established equilibrium, whereas extraction of samples disturbs equilibrium. We are conducting tests under dynamic, rather than equilibrium, conditions; and, therefore, expect different results. Because of the dynamics, the data in the center

portion of the graphs are typically closer to equilibrium conditions than are the data on either end.

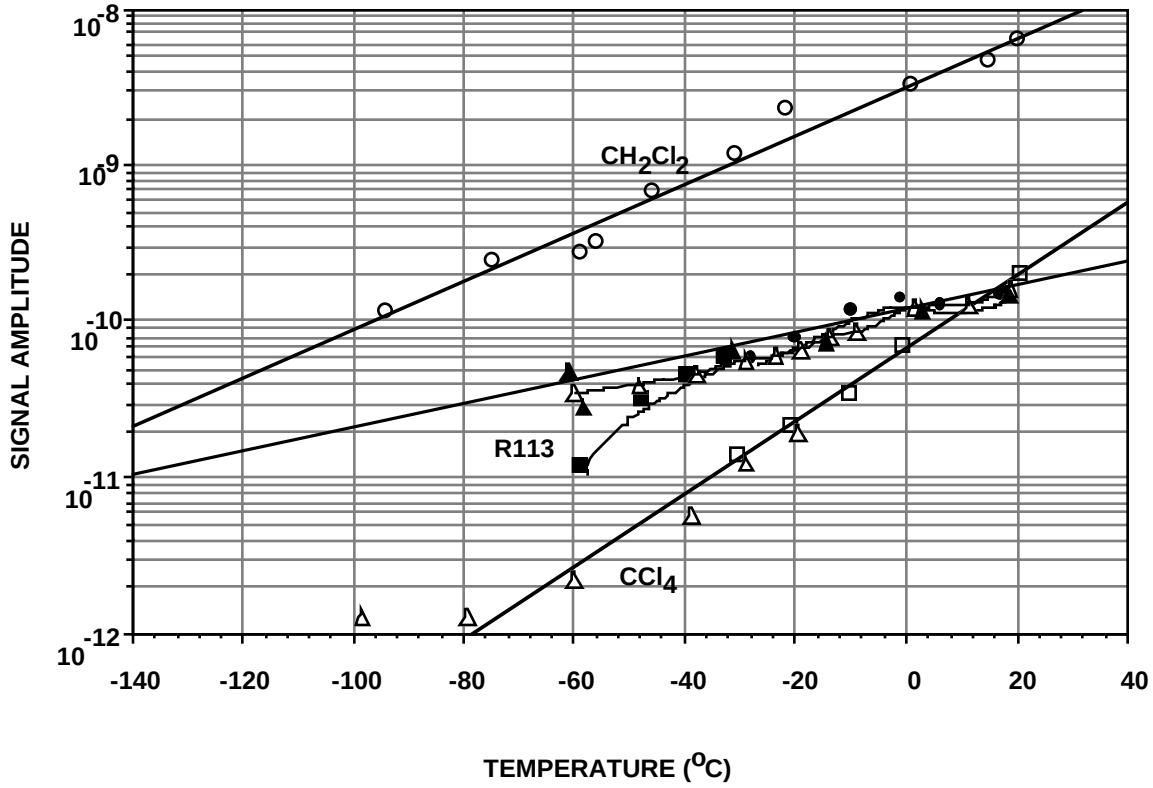

Fig. 2-14. Comparison of signal levels of materials tested.

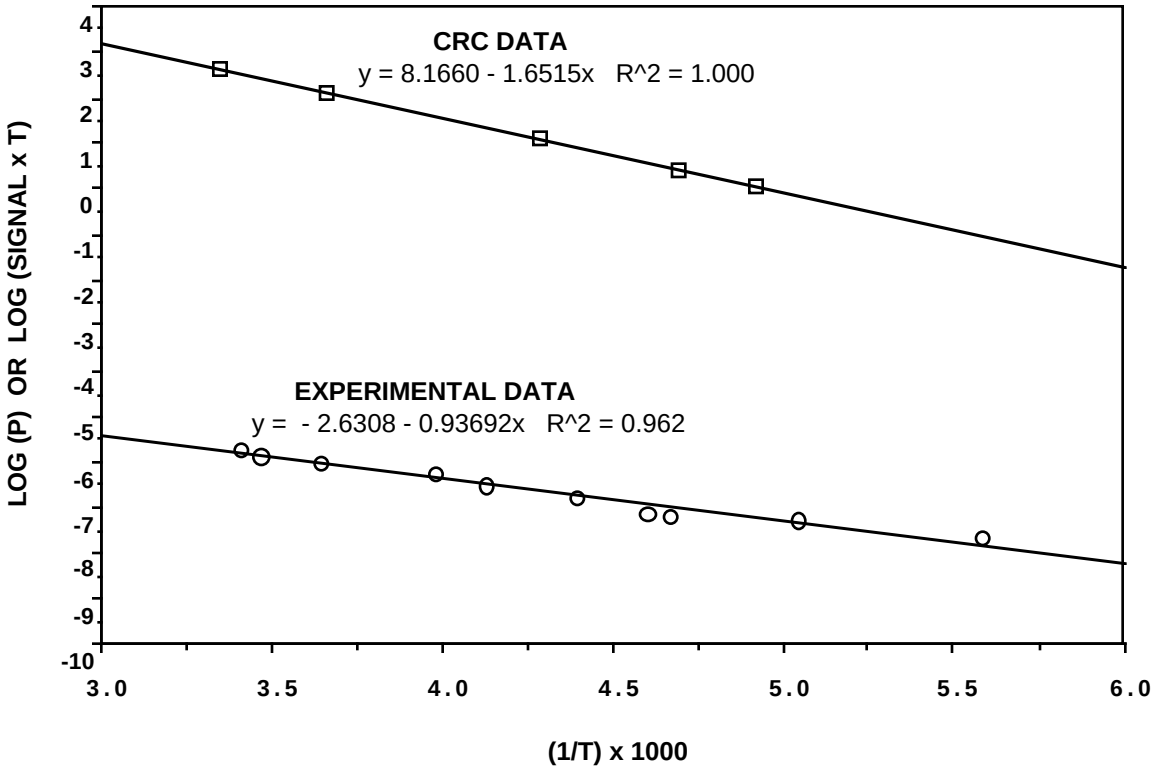

Fig. 2-15. Vapor pressure data for CH_2Cl_2.

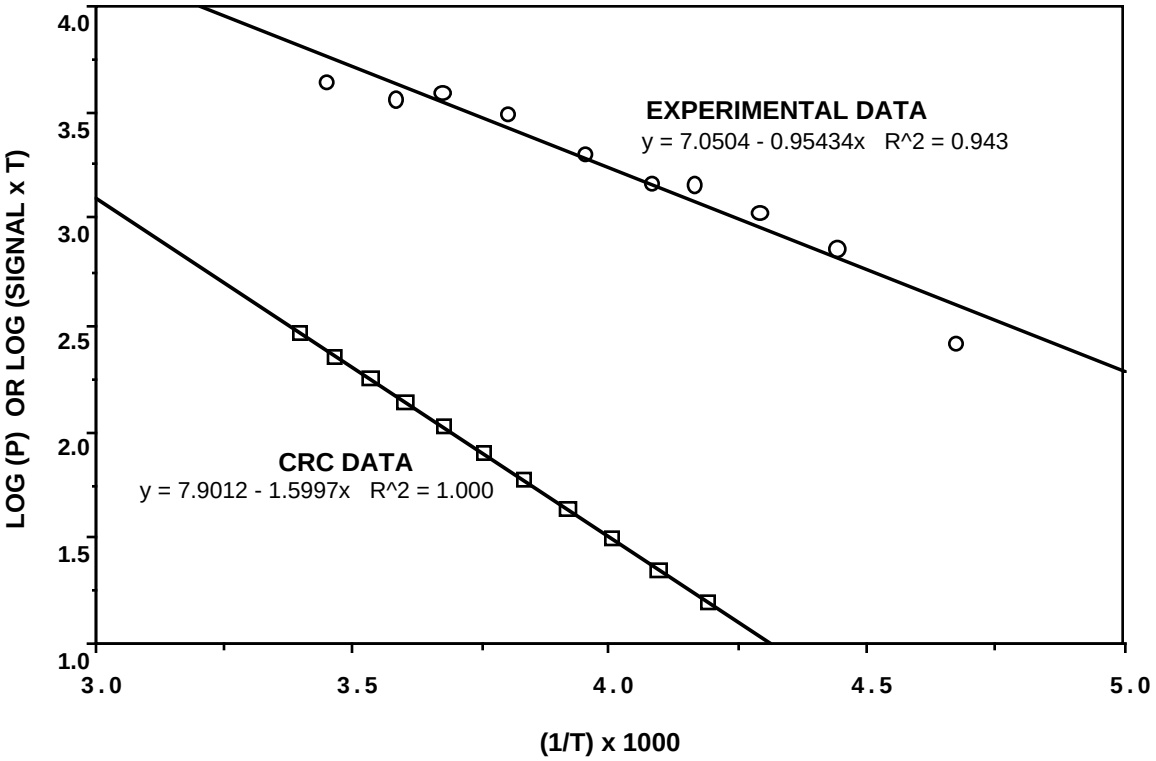

Fig. 2-16. Vapor pressure data for $CCl_2F\text{-}CClF_2$.

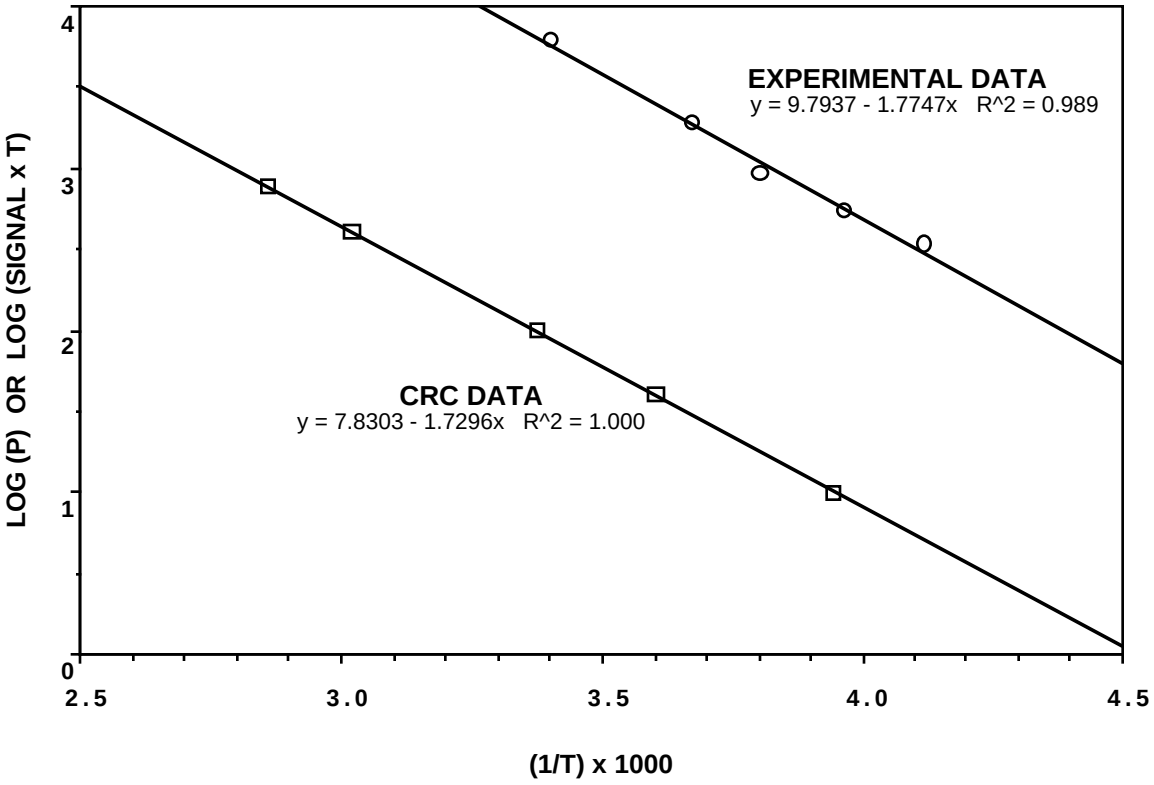

Fig. 2-17. Vapor pressure data for CCl_4.

Known quantities of saturated vapor were carefully injected into the evacuated control-volume sample container, which was then backfilled with air and allowed to stand as a closed system for a predetermined amount of time. A sample was then run through the RGA. A calibration curve using the predominant peaks for each of the three gases (CH_2Cl_2, CCl_2F-$CClF_2$, and CCl_4) related the response of the RGA to ppm levels of the gas. Figure 2-18 shows the results of the correlation. Calibration of the RGA to ppm levels gives an idea of the amount of volatile organic material present. From these tests, we were able to establish the sensitivity of the RGA in the range of 10s to 100s of ppm, the range depending on the solvent. For example, the RGA is more sensitive to CH_2Cl_2 than to CCl_2F-$CClF_2$ (R113). This sensitivity is dependent on the ion framentation of the molecules, the isotopic distribution of the fragments, and the dynamic equilibria of the testing.

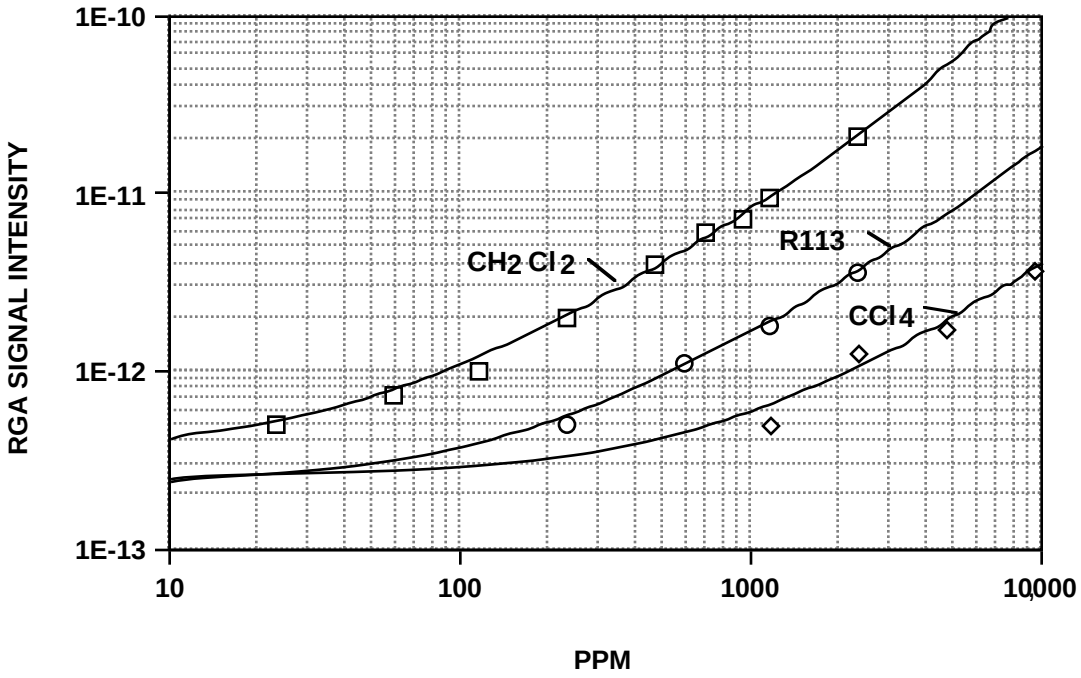

Fig. 2-18. Correlation data for ppm levels of CH_2Cl_2.

2.4.2. Mixed-Materials Tests

The purpose of the next set of experiments was to determine the vapor pressure of the three selected solvents (CH_2Cl_2, CCl_4, and CCl_2F-$CClF_2$) in the various oily mixed-matrix materials that constitute waste at RF. The system setup illustrated in Fig. 2-7 was used to do the evaluation. The three organic compounds were tested with some of the oily mixed-matrix materials, and only the CH_2Cl_2 was tested with all five materials.

We prepared the sample by mixing CH_2Cl_2 into the oil, mixing the oil/CH_2Cl_2 mix into the solid materials (cloth, latex, plastic, Kimwipes®, and Tyvek™). We spread the materials on the base of the control-volume sample container and sealed the system. We did this quickly in order to minimize the release of the organic solvent materials. We included enough oil to be absorbed by or to cover the solid material. Table 2-1 shows the constituent ratios of material, oil, and VOC in the samples. Various tests were performed later on these samples. Additional information in Table 2-1 will be discussed in subsequent text.

Table 2-1. Material Mixes for Volatility Tests

Material/Oil/VOC (quantities in g)	RGA Signal at Beginning	Test Duration (h)	RGA Signal at End
Cloth/oil/CH_2Cl_2 (20/20/5.9)	1.10 × E-09	36	Background
Rubber/oil/CH_2Cl_2 (40/15/5.3)	7.8 × E-10	36	Background
Plastic/oil/CH_2Cl_2 (30/15.4/5.5)	1.38 × E-09	48	Background
Kimwipes/oil/CH_2Cl_2 (10.5/20.2/4.7)	5.8 × E-10	36	Background
Tyvek/oil/CH_2Cl_2 (10.1/20.8/ 5.6)	1.05 × E-09	36	Background
Kimwipes/oil/CCl_4 (10/20.2/5)	1.2 × E-10	—	—
Kimwipes/oil/R113 (10/21/5.6)	1.05 × E-09	20	Indication above background

After the materials were placed at the bottom of the control volume and sealed, the temperature was reduced by chilling the bottom of the control-volume sample container to less than –100°C. To maintain atmospheric pressure in the system, air was allowed into the control volume as the system was cooled. The temperature of the sample was regulated in the control-volume sample container by first chilling an LN_2 dewar and then placing the instrumented control volume inside the dewar. The temperature of the control volume was increased slowly by injection of small quantities of room-temperature air at the bottom of the dewar. The results of those tests are shown in Fig. 2-19, where the signal amplitude for the five mixed-matrix materials is plotted as a function of temperature for the selected mass peaks of the compounds. The sampling for each data point was performed as described in Section 2.4.1. The upper line on Fig. 2-19 is the RGA response for the CH_2Cl_2 by itself and was previously shown in Fig. 2-14. As expected, the signal intensity is lower for mixed-matrix materials with solvents than for the solvents alone.

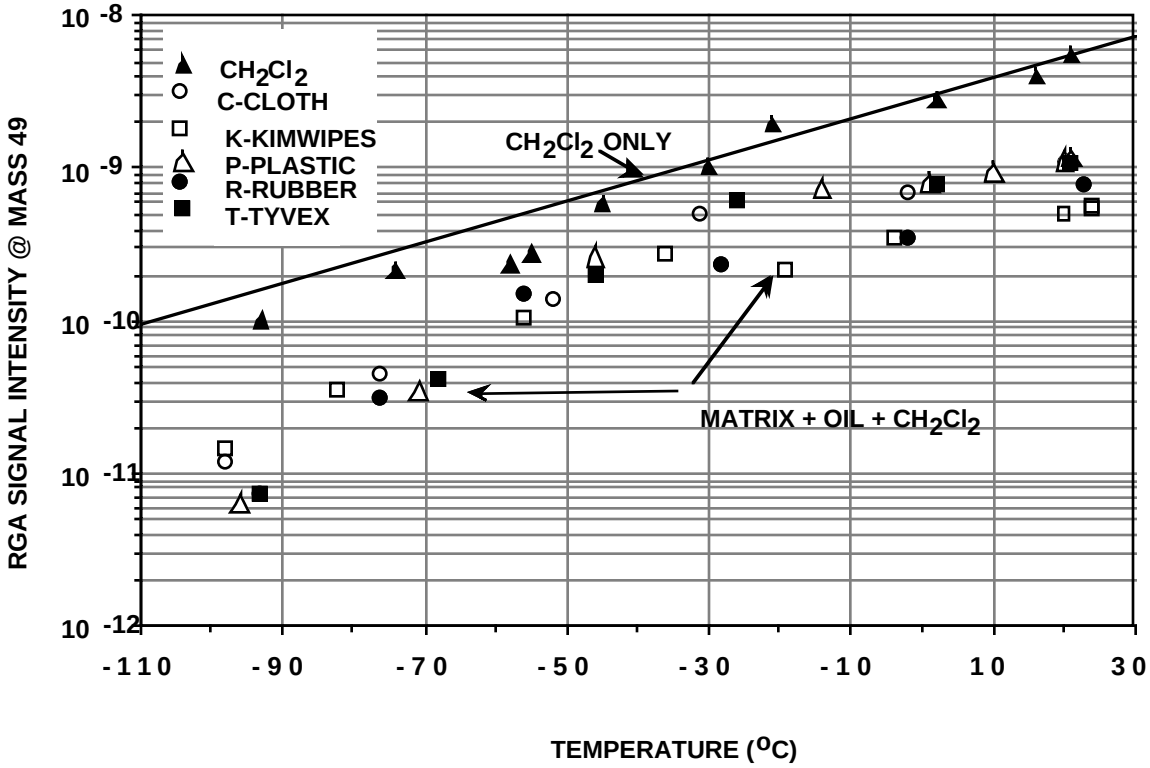

Fig. 2-19. Performance data for CH_2Cl_2.

The two other solvents, CCl_4 and CCl_2F-$CClF_2$ (R113), were tested with only one solid material, Kimwipes. The ratio of oil, Kimwipes material, and VOC is shown in Table 2-1. The results for the two materials are shown in Figs. 2-20 and 2-21. Note that the temperature for these tests is as low as –100°C, and it appears that we observed significant sublimation for the CCl_2F-$CClF_2$ (R113) and the CCl_4. Unlike the results obtained with CH_2Cl_2 as the VOC, the vapor pressures of the CCl_2F-$CClF_2$ (R113) and CCl_4 are not changed significantly when these VOCs are in the oily matrix. In general, the vapor pressures of these solvents are still significant at low temperatures in the oily matrices. We conducted an additional test on the CCl_2F-$CClF_2$ (R113) to evaluate repeatability and determine whether the matrix was saturated or whether the sampling process was depleting the material concentration. Figure 2-20 shows that a second test two hours later gave the same results as the initial test.

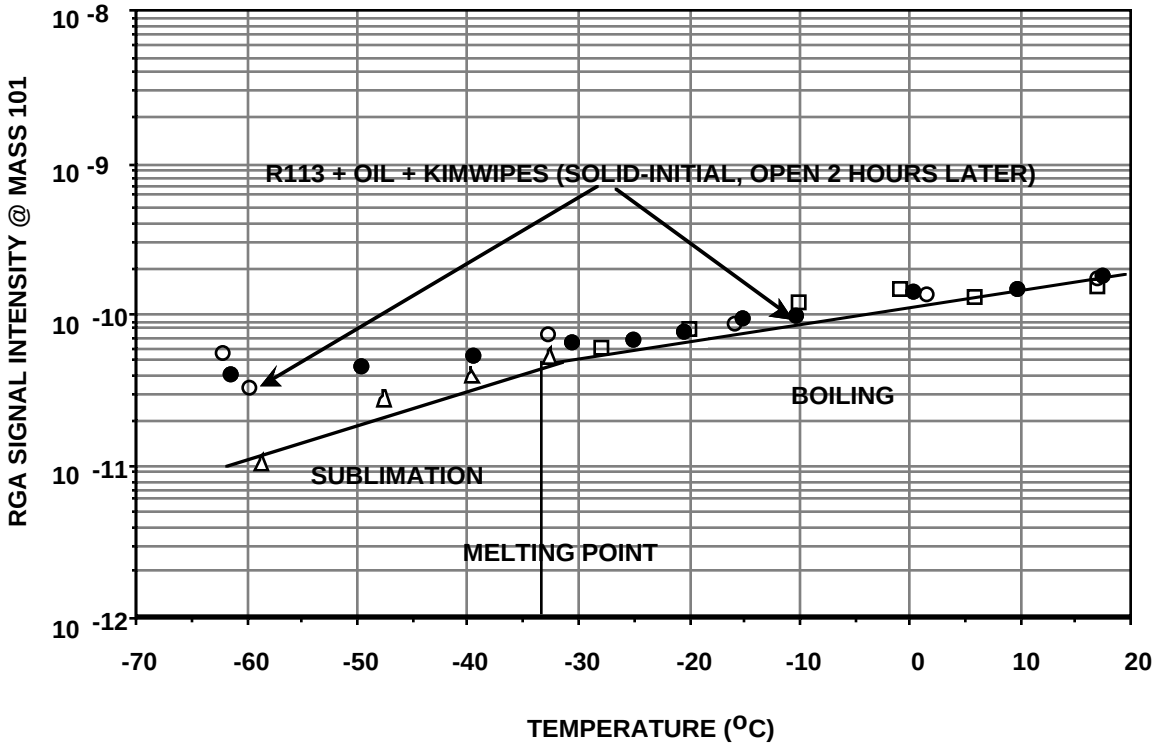

Fig. 2-20. Performance data for $CCl_2F\text{-}CClF_2$.

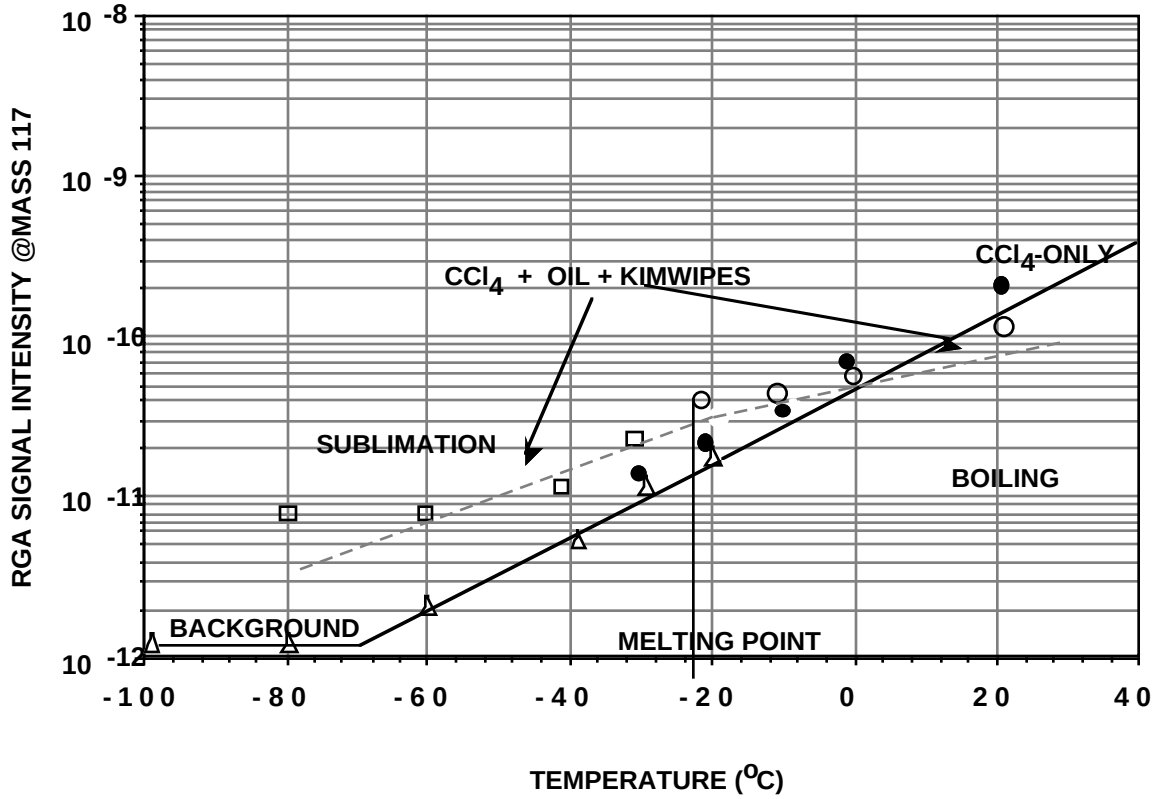

Fig. 2-21. Performance data for CCl_4.

The purpose of the next set of tests for CH_2Cl_2 in the oily cloth matrix was to determine vapor pressure as a function of time at room temperature and at –50°C. In Fig. 2-22, note that the boiling point of CH_2Cl_2 is above room temperature. After 5 min at room temperature, the vapor pressure is reduced by an order of magnitude; but it takes approximately 30 min to achieve a similar result at –50°C. Because the solvent concentration can be related directly to the vapor pressure, the lowering of the vapor pressure equates to a loss in concentration in the matrix. This argument also follows from the higher vapor pressure at –50°C at later times compared with the vapor pressure at room temperature.

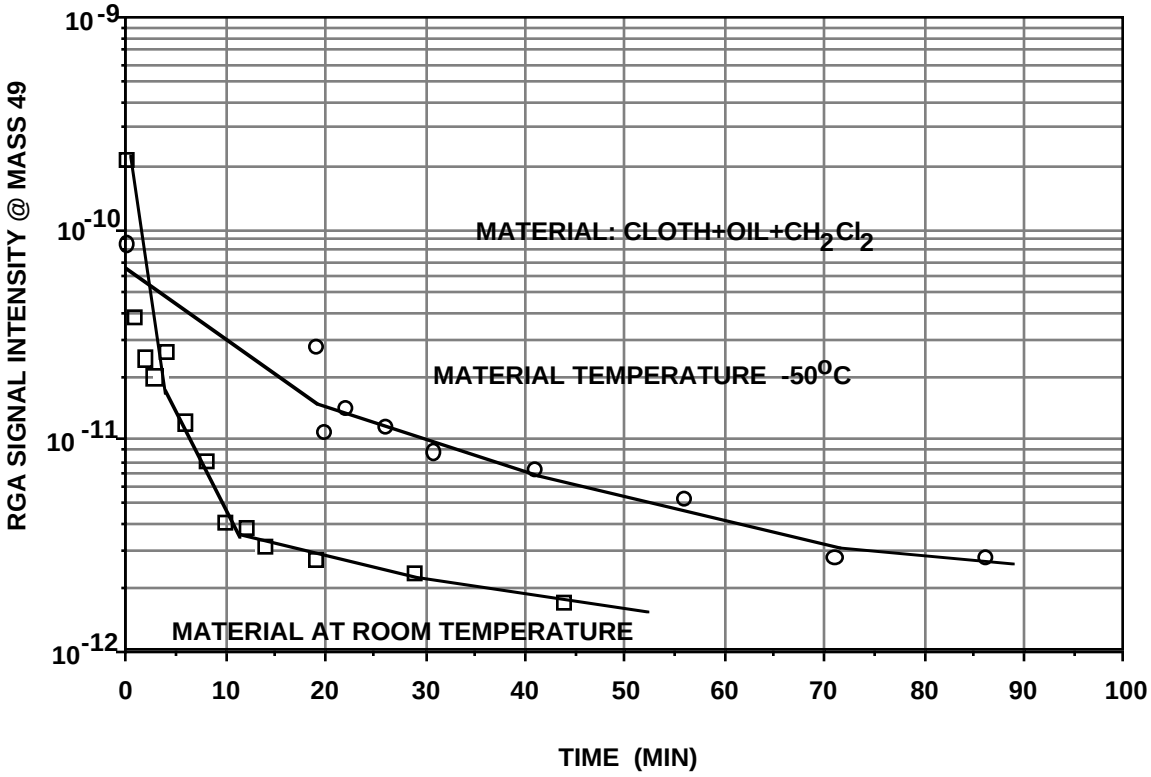

Fig. 2-22. Evaporation rate of CH_2Cl_2 in oily cloth matrix.

Additionally, we checked the vapor pressure of CH_2Cl_2 in the five matrix materials and that of CCl_2F-$CClF_2$ (R113) in oily Kimwipes. These checks were made after the materials had been placed in unsealed plastic bags for 20–48 hours. After these time periods, no mass spectrum could be obtained (see Table 2.1). As indicated in Fig. 2-18, for CH_2Cl_2 the sensitivity is about 20 ppm, and for CCl_2F-$CClF_2$ (R113) it is about 200 ppm.

2.4.3. Shredder Tests

We combined the cryoshredder that we built to do the volatility studies (see Fig. 2-1) with the paddle-wheel mixer we used in Task 1. We used thermocouples in numerous locations to measure temperatures and used LabVIEW software to collect data. Figure 2-23 shows the LabVIEW template used to display temperature measurements with thermocouple placement during the experiments.

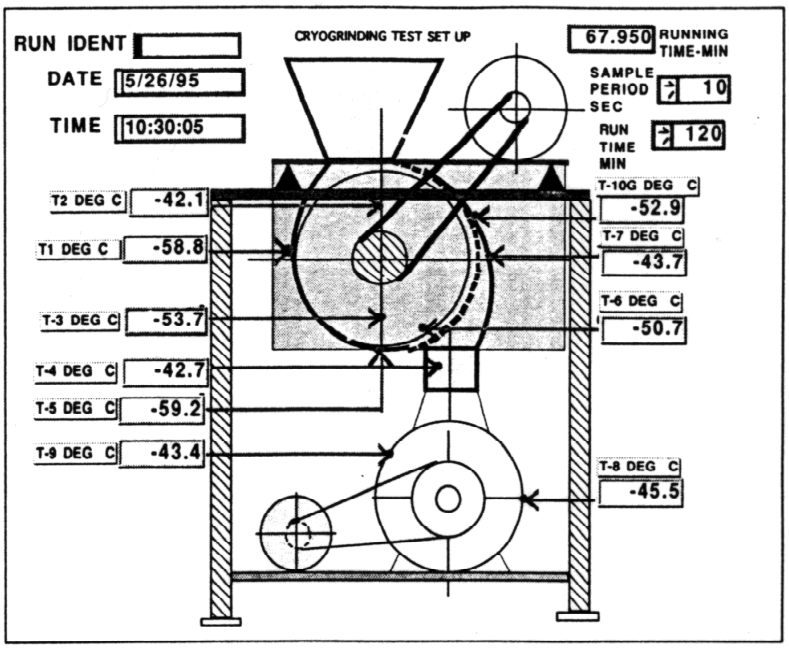

Fig. 2-23. Sample LabVIEW© template during data collection.

The system was set up to do gas sampling during the cryogenic grinding, as well as sampling with the RGA, which had been previously used to estimate the quantities of constituents in the various mixed-matrix materials. Staff of LANL's Chemical Science and Technology (CST) Division established the procedure for sampling for the volatile solvent and the solvent in the solid. They also followed the procedural guidelines described in the original test plan for Task 2 agreed upon between DOE, National Institute of Standards and Technology (NIST) at Boulder, and LANL. Figure 2-24 shows the system setup and the sampling locations.

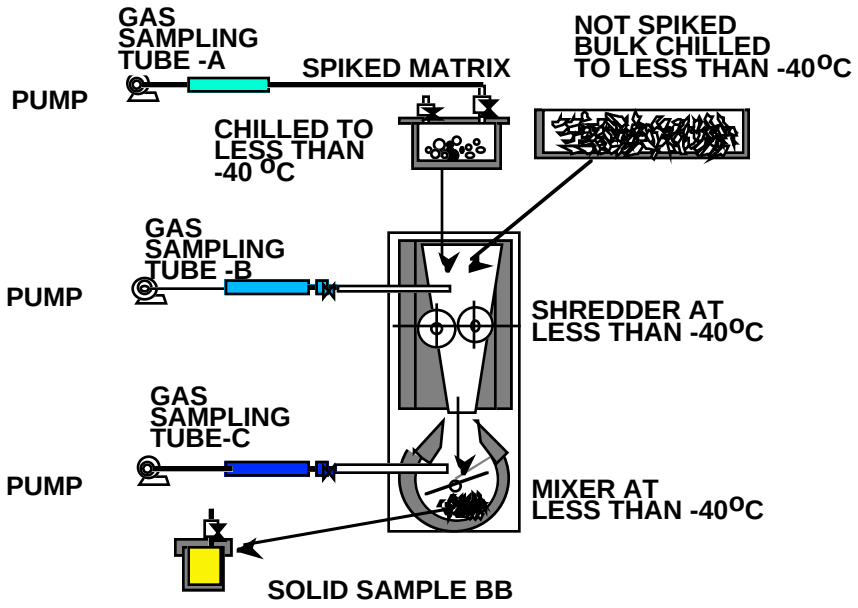

Fig. 2-24. Locations for sampling VOC during cryogenic grinding.

Table 2-2 shows the types and quantities of constituents forming the two mixed-matrix materials for which CH_2Cl_2 was evaluated in accordance with the following procedure:

1. Liquid CH_2Cl_2 combined with vacuum pump oil was mixed with the solid material in the ratios shown in the first column of Table 2-2. The resulting mixture was quickly placed in the bottom of the same control-volume sample container used in conjunction with the RGA. The sample container was then cooled to less than –40°C; and the temperature was monitored, as previously described.

2. After steady-state temperatures had been reached, gas samples (denoted as Sample A) were extracted through the VOST into sorption tubes.

3. The shredder and mixer were turned on. The shredder operated at about 1100 rpm and the mixer at 90 rpm. The temperature of the system was established at less than –40°C by LN_2, which was poured into the inlet of the shredder. The metal and gas temperatures were recorded throughout the process.

4. Half the volume of the noncontaminated material (cloth or Tyvek) was chilled, using LN_2, and then run through the shredder.

5. After half of the noncontaminated material was shredded, the contaminated sample was quickly poured out of the chilled control-volume sample container and into the shredder. When the RGA indicated the presence of the CH_2Cl_2, a gas sample (denoted as Sample B) from the top end of the shredder was extracted through the VOST. This step in the process normally takes about 5 minutes.

6. The remaining half of the chilled noncontaminated material was passed through the shredder, and the mixer was allowed to run until most of the material appeared to have passed from the shredder into the mixer.

7. Five minutes after the shredding process stopped, with the mixer still running and both mixer and material chilled to less than –40°C, another gas sample (denoted as Sample C) was extracted through the VOST.

8. Finally, the system was turned off; and a solid sample (denoted as Sample BB) was extracted from the mixer and placed in a 1-L sealed container fitted with two gas valves.

We used this process first with the cloth material and later with the Tyvek material. To make it easier for the materials to pass through the 0.375-in. screen in the shredder, we preshredded them into somewhat smaller pieces using a material slicer. The shredder used in the test produced cotton-like particles from both the cloth and the Tyvek materials during the cryogrinding process. However, one would not expect to preshred items with the system being developed by DOE, RFETS, and NIST.

Table 2-2. Mixed-Matrix Materials in Shredder and Mixer and RGA Signals

VOC/Material/Oil Mix (ratio in g)	Quantity in Shredder (g)	Quantity in Spike (ppm) Calculated	Quantity in Mixer (ppm) Calculated	RGA Signal
CH_2Cl_2/cloth/oil (2.7/40/20)	740	45,000	3650	1.8×10^{-11}
CH_2Cl_2/Tyvek/oil 1.3/40/20	490	21,700	2650	1.3×10^{-11}

Figures 2-25 and 2-26 show strip-chart data as a plot of temperature vs time for the cloth and Tyvek materials, respectively. The chart begins when Sample A was taken, and the chart ends before the material was dumped into the shredder.

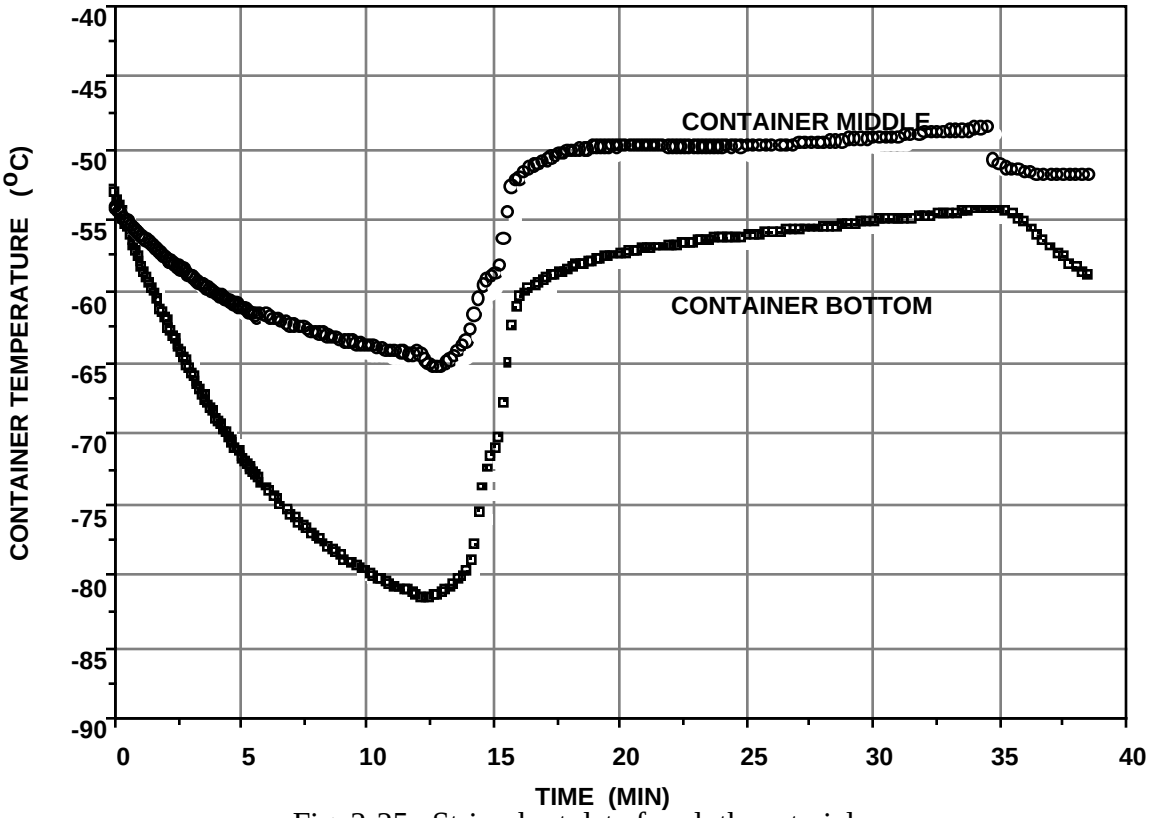

Fig. 2-25. Strip-chart data for cloth material.

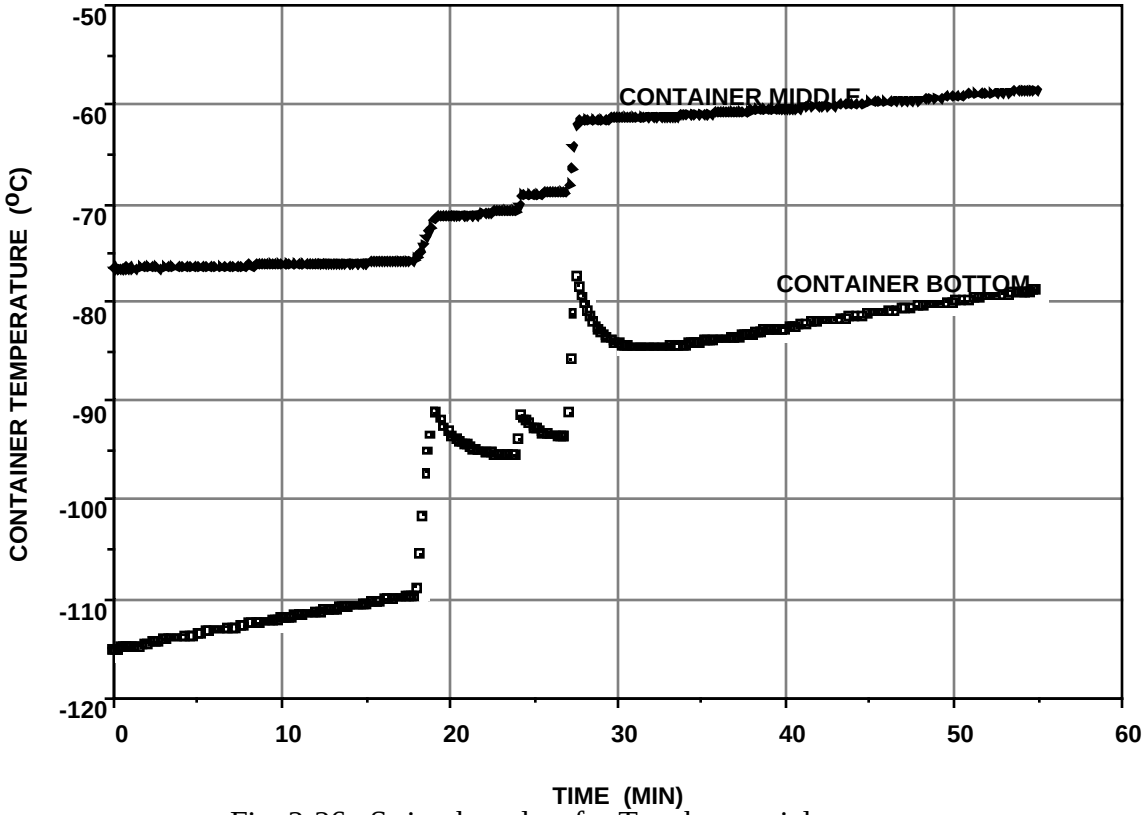

Fig. 2-26. Strip-chart data for Tyvek material.

Figures 2-27 through 2-29 show the time-and-temperature profiles for the shredder metal and gas temperatures during the test operations with Tyvek material. Note that the system is operating at temperatures less than –40°C. Operation at such low temperatures was a primary objective in the test plan for Task 2.

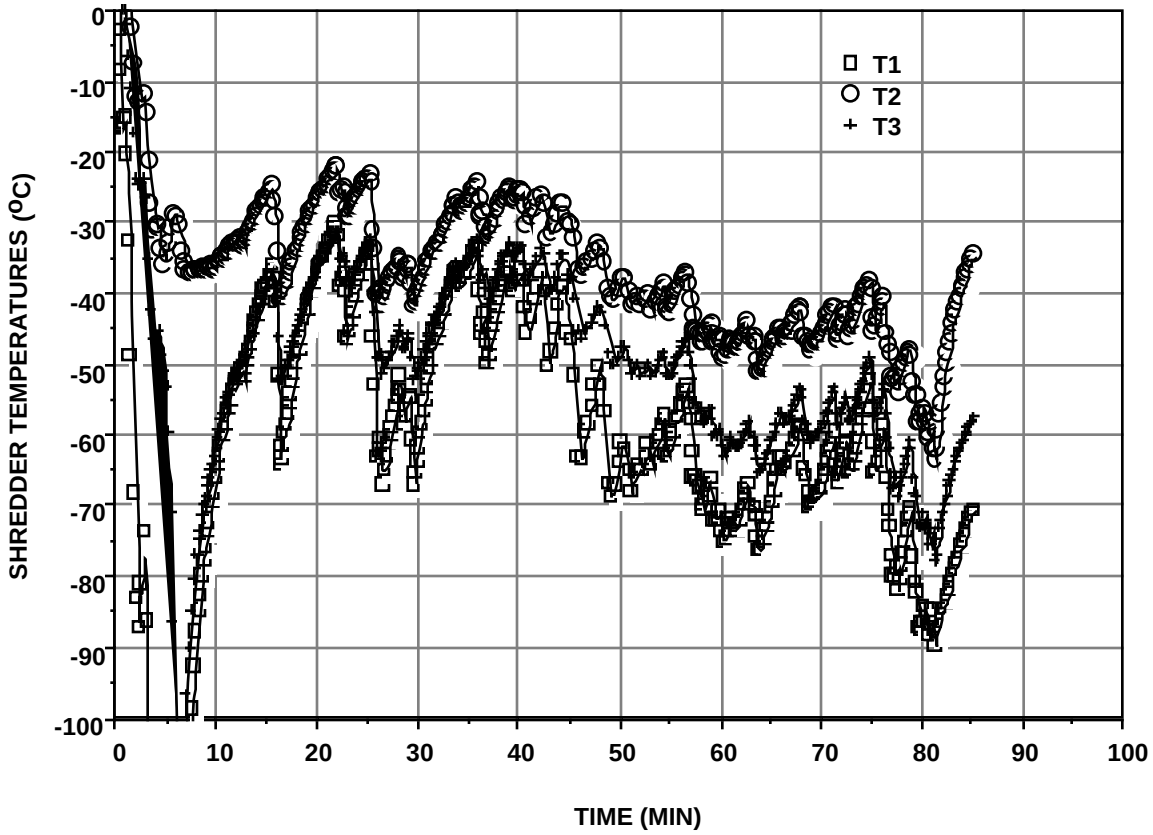

Fig. 2-27. Shredder temperatures during test operations with Tyvek material.

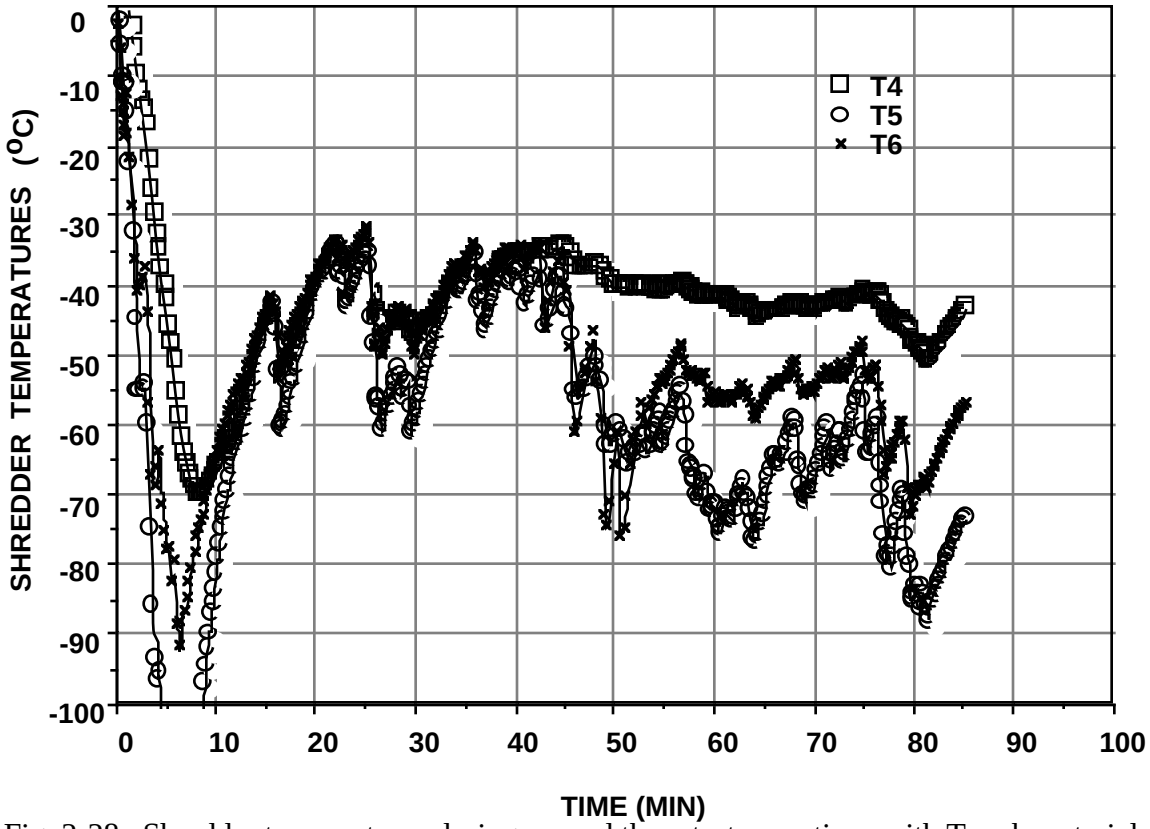

Fig. 2-28. Shredder temperatures during second three test operations with Tyvek material.

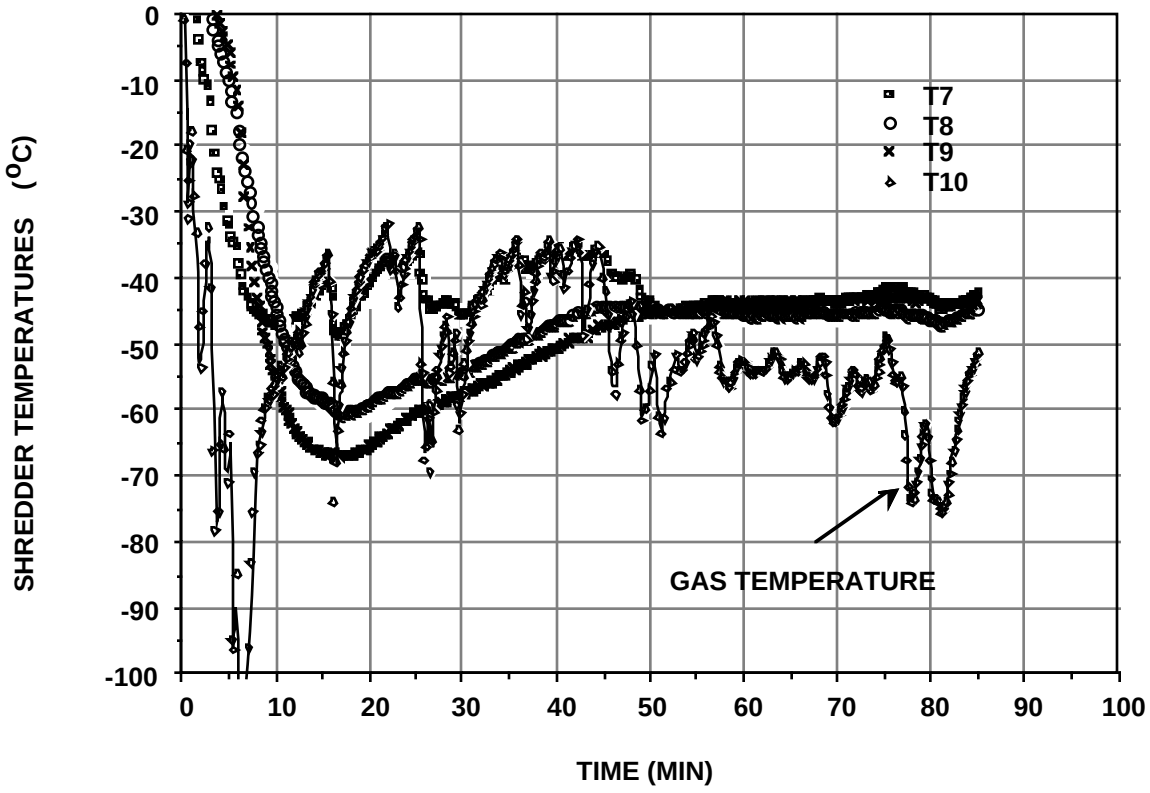

Fig. 2-29. Shredder metal and gas temperatures during Tyvek material test operations.

2.4.4. Sampling Methods

This section presents the results of gas sampling and gas chromatography. The following tables show the results of the gas analysis performed by staff in LANL's Organic Analysis Group (CST-12). Table 2-3 shows the results of the cloth shredding test. Two gas samples for each location were taken from the desorption tubes. One would indicate high levels of organic compounds; the other, low levels of these compounds. The low-level sample tube was saturated because of the large quantity of organic materials spiked into the sample. Table 2-2 shows the calculated quantity of the organic material in both the spike material and the bulk in the mixer after shredding.

Table 2-3. Results of Gas Chromatography Analysis of Shredded Cloth Samples

Sample ID	Sample Location	Temperature (°C)	Material Tested	Analysis Gas	Results (μg/L)
AAC4373	A	–50	CH_2Cl_2 in cloth/oil	CH_2Cl_2 (high levels)	61,000 (19,000 ppm)
AAC4374	A	–50	CH_2Cl_2 in cloth/oil	CH_2Cl_2 (low levels)	Saturated
AAC4375	B	–40	CH_2Cl_2 in cloth/oil	CH_2Cl_2 (high levels)	27,000 (8,400 ppm)
AAC4376	B	–40	CH_2Cl_2 in cloth/oil	CH_2Cl_2 (low levels)	Saturated
AAC4377	C	–40	CH_2Cl_2 in cloth/oil	CH_2Cl_2 (high levels)	15,000 (4,800 ppm)
AAC4378	C	–40	CH_2Cl_2 in cloth/oil	CH_2Cl_2 (low levels)	Saturated

Table 2-4 shows the results of shredding Tyvek material. Only one sample was taken at each location. The quantity of Tyvek material detected is lower than the quantity of cloth material detected, because less CH_2Cl_2 was added to the Tyvek material.

Table 2-4. Results of Gas Chromatography Analysis of Shredded Tyvek™ Samples

Sample ID	Sample Location	Temperature (°C)	VOC Tested	Analysis Gas	Results (µg/L)
AAC4379	A	–50	CH_2Cl_2 in Tyvek/oil	CH_2Cl_2 (low levels)	26,000 (8,300 ppm)
AAC4380	B	–50	CH_2Cl_2 in Tyvek/oil	CH_2Cl_2 (low levels)	21,000 (6,700 ppm)
AAC4381	C	–50	CH_2Cl_2 in Tyvek/oil	CH_2Cl_2 (low levels)	5,700 (1,800 ppm)

A sample of solid material taken during each test operation was tested for CH_2Cl_2, as described in step B, and a sample was extracted when the mixed-matrix materials were being prepared (see Fig. 2-19). Because the first two samples were sealed in a closed container, the gas contained within the matrix material was released into the container when the samples were warmed to room temperature. The gas in the container (head space) was analyzed to determine the amount of gas left in the sample after the shredding operation. Concentrations of CH_2Cl_2 were detected in the cloth sample, but the Tyvek sample was lost during the chemical analysis process. Table 2-5 presents the results of gas chromatography analysis of the solid materials. The first two were from the shredding operation and the last from a solid sample that had been partially exposed to the atmosphere for 14 days.

Table 2-5. Results of Gas Chromatography Analysis of Solid Samples

Sample ID	Sample Location	Temperature (°C)	VOC Tested	Analysis Gas	Sample Size (g)	Results (µg/L)
AAC4382	BB	20	CH_2Cl_2 in cloth/oil	CH_2Cl_2 in head-space cloth	16	49
AAC4383	BB	20	CH_2Cl_2 in Tyvek/oil	CH_2Cl_2 in head-space Tyvek	15	lost in shredder 2.9
AAC4384	—	20	CH_2Cl_2 in cloth/oil after 14 days	CH_2Cl_2 in cloth	40	2.8

The original quantity of 740 g of cloth was spiked with 3,650 ppm of CH_2Cl_2. In analyzing the first sample of Table 2-5, we found the 16 g of cloth to contain 49 ppm of CH_2Cl_2. It appears that only about 2,300 of the original ppm was accountable (740 g divided by the 16-g sample times the 49 ppm detected at the end equals 2,266 ppm). The quantity of

2,300 is about two-thirds of the original. In the Tyvek sample, the original quantity of CH_2Cl_2 was 2,650 ppm loaded in a material of 490 g of Tyvek. The comparison was done as above for the second sample of Table 2-5. It appears that only about 98 ppm of the original material was recovered after the shredding operation. A number of factors may contribute to the reduced quantities of VOCs after shredding.

2.5. Conclusions

Separate regimes for the operation of the complete system should be considered as an option for addressing volatility concerns. The RGA results show that the oily-matrix materials will in a very short period of time (5 min) at room temperature release a significant quantity of solvent as gas (see Fig. 2.21), even when that solvent has a relatively high boiling point—one above room temperature. Therefore, even when the cryogenic shredder is operated at –40°C, a significant amount of solvent material volatilizes during the opening of the drums and bags containing the materials and during the warmup process when the materials are being repackaged. Thus, the release of VOCs during shredding may, in fact, be a moot issue because such compounds readily are released at room temperature during other parts of the operation. In any event, because a significant amount of vapor pressure occurs for a large number of VOCs at and below –40°C, on-line monitoring for solvents, as part of the glovebox system, may be a way to capitalize on their volatility. Screening materials during processing will enable us to determine whether an RGA system should be used to determine their VOC contents.

The boiling points of some VOCs are so low (less than room temperature for CH_3Cl) that these VOCs cannot be loaded effectively into a matrix material for testing. Those who performed the gas and solid testing, as well as other specialists throughout LANL, were challenged to devise an appropriate method to load these high-vapor-pressure species into the predetermined matrix materials; but no such method has been presented yet. Further consideration of low-boiling-point species requires identification of the exact matrix in which they can be found. Some of the species may be generated by radiolytic decay of plastics or may exist as a component in the production of the plastic.

Additionally, those solvents with relatively high boiling points are likely to benefit most from cryogenic shredding and mixing because these operations last a long time in comparison to the time required for unpacking and packaging operations.

Material balances in an open system have become a difficult task, as can be seen from the scatter of the data. The results of these tests are trends that can aid understanding material-handling requirements in a cryoshredding operation. For example, the VOC cannot be tested during shredding.